INHIBITION OF ANTIMONY SULPHIDE SCALE BY CHEMICAL ADDITIVES: LABORATORY AND FIELD TEST RESULTS

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ABSTRACT

The PC-26 well, the first exploratory deep well in the Piancastagnaio field (Mt. Amiata area), was drilled at the end of the 1970s. It started production in 1980. Heavy scaling problems were soon experienced; these started a few meters downhole in the production casing, and occurred mainly inside the pressure separator.

This scale consisted mainly of antimony sulphide and amorphous silica, with the latter prevailing in the low-temperature part of the separating equipment.

The aim of the first laboratory tests was to screen possible chemical additives capable of inhibiting the sulphide scaling and to develop effective concentrations of the most promising products.

In subsequent field tests two selected inhibitors were both effective in preventing antimony sulphide scaling, although with different side effects on silica precipitation.

Since these positive field test results, an inhibitor addition has been used in the PC-26 well, and it is no longer subject to any appreciable operating problem deriving from scale build-up in the surface plant.

1. INTRODUCTION

The first deep exploratory well in the Piancastagnaio field (Mt. Amiata area) was drilled in 1979 with the aim of verifying the presence of fractured layers inside the metamorphic basement underlying the shallow reservoir (Triassic carbonate-evaporitic fomiation) on exploitation since 1962.

The well, named Piancastagnaio 26 (PC-26), crossed a practically impermeable basement (mainly quartzite and phillite Paleozoic formations) up to a depth of 2800m, where a fractured layer was found with liquid phase at a pressure of 20 MPa and a temperature of 330°C. The chemical composition of the liquid phase discharged by the atmospheric separator is given in Table 1. Silica and antimony contents estimated at reservoir conditions are, respectively, about 700 and 50 mg/l.

Table 1. Analysis of the brine discharged by the atmospheric separator

Alkalinity	meq/l	6.1
Na	mg/l	446
K	mg/l	109
Cl	mg/l	731
H2S	mg/l	5.1
H3BO3	mg/l	3570
As	mg/l	19
NH4	mg/l	71
SiO2	mg/l	1140

The preliminary tests showed that, despite the limited permeability-thickness product of the deep layer (about 0.1E-12 m^3), the well was a commercial producer because of the high reservoir pressure and temperature.

A pressure separation plant was then installed and since 1980 the well has been linked to the Piancastagnaio 2 power plant for an extended testing period aimed at evaluating the trend of production parameters and the chemical-physical characteristics of the produced fluids. The total production was about 15 kg/s with only 10% in weight of liquid phase, because the flash occurred inside the formation.

After a few months of production, heavy scaling problems were experienced. These started a few meters downhole in the production casings and mainly inside the pressure separator, as well as in the atmospheric separator. It was here that the liquid phase was flashed before being stored in a settling tank and piped to the reinjection wells.

The scaling consisted mainly of antimony sulphide and amorphous silica, with the latter prevailing in the low-temperature section of the separating equipment.

Silica deposition was probably started by the antimony sulphide precipitation, whose solid particles acted as deposition nuclei, thus favouring amorphous silica scaling in the high-temperature part of the separating equipment.

The reduction of the flowing area of the pipes caused by the scale and the consequent pressure drops gave rise to periodical (after 8 to 10 months of operation) outages of the plant for cleaning operations, which required closure of the well. The associated production **loss** lasted about one week and some pipes had to be replaced. Moreover, the operation of the plant was severely hindered by the effect of the scale on the valves, which remained blocked and leaked when shut.

During the above mentioned tests, two more deep exploratory wells were drilled in the same area with positive results. The presence of an extended deep reservoir with a pressure and a temperature similar to the ones measured in the PC-26 well was thus confirmed.

A development program of the field was accordingly outlined, foreseeing an overall activity which included the drilling of 50 wells and the installation of 7 new power plants of 20 MW each.

The scaling problems experienced during the PC-26 well testing had yet to be solved, and it was expected that the new wells would have the same problems as PC-26, if the chemical composition of the deep reservoir were uniform, resulting in costly drawbacks in the operation of the plants.

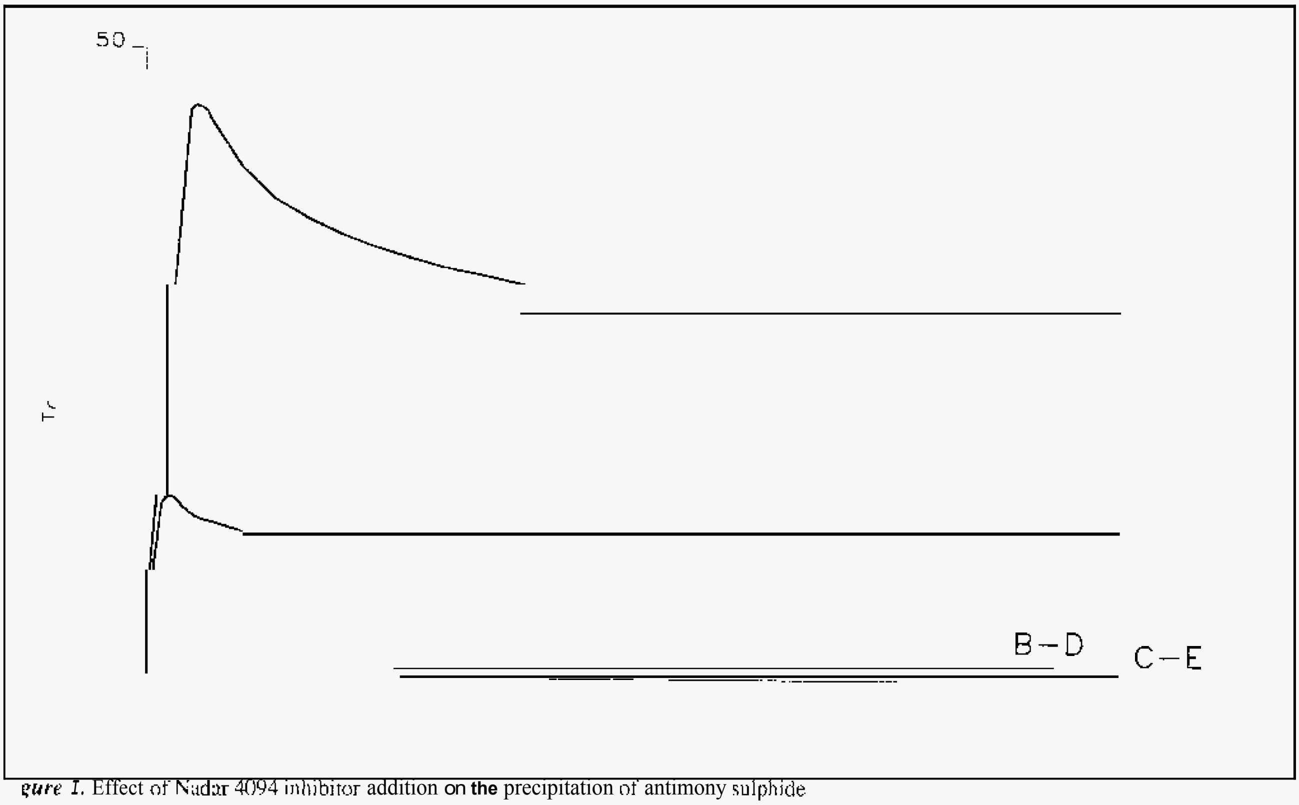
Based on the positive results previously obtained in the control of the carbonate scale with chemical inhibitors (Corsi ***et al.,*** 1985; Pieri *et al.*, 1988), a study was started with the aim of identifying possible chemical additives able to prevent the precipitation of antimony sulphide and, consequently, of amorphous silica. Such research activity was carried out with laboratory tests as the first step, and then with field tests.

2. LABORATORY TESTS

2.1 Experimental

The laboratory tests were carried out as a preliminary screening of selected products that were currently used for scale control and water treatment: Albright Briquest ZN31-25S; BP Breox 3400, 8000, 12000; Cyanamid Cyanamer P80 and P70, Aerofloat 249 and 425, Xantate 317; Degussa POC 2020, POC P, 1189, 1389; Imco Poly RX; Monsanto Dequest 2006, 2010 and 2066 Montedison/Arca Ecopol 4013, 5002 and 5004; Nadar 1008, 1018, 1045, 1046, 4091, 4092, 4093 and 4094; Pfizer Flocon 100; Protex Aquaprox MD 1030.

The following low-temperature batch test methodology was used: stock solutions [0.0005 M] of the soluble salts, antimony(III) chloride



gure 1. Effect of Nadar 4094 inhibitor addition on the precipitation of antimony sulphide

and sodium sulphide, were prepared in distilled water containing sodium chloride [0.1 M] from analytical grade chemicals and filtered through membranes (Millipore, 0.45 μm). The dissolution of antimony was made easier by adding tartaric acid [0.0005 M] and adjusting to the desired value of pH (~5.5) with a concentrated NaOH solution.

The spontaneous precipitation was started by the quick addition of the sulphide solution (40 ml) to an equal volume of the antimony solution, containing *the* additive. The resulting final pH *of* the suspension was about 6.5.

The progress of precipitation was continuously monitored under vigorous stirring by a Metrohm E 1009 photometer recording the values of transmittance at λ=600 nm.

At the end of the precipitation (20-30 minutes), the suspension was filtered (0.45 μm) and the filtrate analyzed for antimony concentration by atomic absorption.

The organic additives were dissolved, as received, in distilled water (5-10 g/l) and added at the test concentrations to the antimony solution 2 minutes before mixing with the sulphide solution.

The thermal stability of the additives (required to allow downhole injection) was tested by heating their concentrated solutions (100 g/l) in an autoclave at 200°C under stirring (about 85 minutes were needed to reach this temperature, maintained for 15 minutes: air cooling to room temperature required 30 more minutes).

The heat-treated solutions were used to repeat the spontaneous precipitation tests previously described.

2.2 Results

The unseeded spontaneous precipitation of antimony sulphide, as decribed in the previous section, proved to be a useful method for the screening of the additives.

The progress of the precipitation is shown by the typical transmittance curves of Figure 1: in the absence of inhibitor (curve N), many fine particles of Sb_2S_3 instantaneously form after the mixing of the solutions, with a sharp decrease of transmittance; precipitation is thus nearly completed after about 2 minutes. Slow coagulation of the particles in larger aggregates then takes place, with an increase of the transmittance to a steady value

The amount of colloidal particles decreases with the addition of 31.2 ppm of Nadar 4094 inhibitor (curve A). The precipitation is completely inhibited (curves B-D and C-E) at higher product

Table 2. Laboratory test resulrs. Inhibitors effectiveness is shown by
ie amount of antimony that remains in solution after 20-30 minutes.

ADDITIVE	ACTIVE PRODUCT CONTENT*	CONCENTRATION mg/l	ANTIMONY IN FILTERED SOLUTION WITH UNTREATED ADDITIVE mg/l	ANTIMONY IN FILTERED SOLUTION WITH TREATED ADDITIVE* mg/l
Blank	-	-	5.0	-
Nadar 4091	20	62.5	7.5	-
		125	7.5	-
		250	8.0	-
		500	9.0	7.0
		1000	-	7.0
Nadar **4092**	33	75	2.5	-
		150	6.1	-
		300	32.0	30.5
		600	32.5	-
Nadar 4093	40	62.5	5.8	-
		125	15.2	-
		250	24.4	13.2
		500	30.0	28.0
Nadar 4094	40	31.2	9.5	-
		62.5	29.6	30.0
		125	31.8	32.0
Nadar **4095**	25	120	25.0	20.2
		200	29.0	28.7
Degussa 1389	33	45	4.0	
		90	26.2	
		180	30.0	4.0
		540	-	5.0
Degussa 1189	33	90	4.5	
		180	30.1	5.0
		540	-	4.0
Nadar 1602	20	100	22.0	25.7
		200	29.5	30.5
nco Poly RX		200	11.7	-
		300	12.2	-
		400	16.0	-
***	-	-	35.0	-

% by weight in the commercial chemical

' Heating at 200°C (*see* text)

'' Concentration in the initial solution (without precipitation) concentrations (62.5 and 125 ppm): all the antimony remains in solution after 30 minutes.

This behaviour, common to other effective additives and typical of the formation of amorphous precipitates, is quite different from that observed for the calcium carbonate system, where threshold concentration of inhibitors (0.2-2 ppm) caused a marked increase of the induction time required for the onset of precipitation and a reduction of the crystal growth rate.

In fact, none of the additives used as inhibitors for the carbonates (phosphonates, acrylates, carboxylates) proved effective in this case.

Table 2 summarizes the results obtained in the laboratory tests for the additives effective in preventing antimony sulphide precipitation. The minimum concentration needed to maintain a clear solution (transmittance >98%) and the final concentration of antimony in solution are also shown.

Nadar 4091 additive showed the typical behaviour of a dispersing agent: the solution treated with this product maintains a high transmittance (80-90%), but with a very low concentration of antimony in solution. The resulting colloidal dispersion remains stable for many days.

Probably, the other proprietary polymers supplied by Nadar and Degussa are able to complex the antimony ion in solution: a high concentration is thus needed in order to inhibit the precipitation.

The reduced scaling capacity observed in the treated solutions is also connected with the modified crystal structure induced by the adsorption of the organic additives.

Precipitated amorphous antimony sulphide obtained by operating with larger volumes of solutions (with and without the addition of Nadar 4094) was filtered, washed, dried and examinated by EDS and XRD techniques.

The solid precipitated from untreated solutions is acicular and crystallizes as black stibnite after heating at 190 C; the addition of Nadar 4094 produced a granular precipitate that remains stable despite heating at high temperature (Figure 2).

The thermal treatment of the inhibitors shows that many organic compounds (Nadar 1389, 4091 and 4093; Degussa 1189 and 1389) completely decompose and become ineffective; however, even though they cannot be injected downhole, their use at higher concentrations in the geothermal facility at the surface remains feasible.

On the basis of the laboratory tests, Nadar 4094 and 1602 were considered the most promising additives (Nadar 4092 is available on request, but only in large quantities). However, Degussa 1389 was also considered worthy of field testing, as it was specifically formulated as a silica scaling inhibitor.

Nadar 4094 is an omopolymer with amine groups, while Degussa 1389 is a copolymer with carboxylic and amine grups.

3. FIELD TESTS

3.1 Experimental

Field tests of the inhibitors were carried out at the PC-26 well, which had remained closed for two years after the end of the first long-term production tests.

The scheme of the separating plant installed and used for the experimentation is shown in Figure 3. The two-phase fluid is separated by a pressure separator operating at 1-1.1 MPa: steam is directed to the Piancastagnaio 2 power plant, while the residual brine is piped to the reinjection system after flashing at atmospheric pressure.

The scaling rate was determined by measuring the thickness of the deposits formed on the pipe sections immediately downstream from the orifice plates (d/D = 0.5) installed within inspectionable bypass loops. Three bypasses were purposely installed: upstream and downstream from the pressure separator and downstream from the atmospheric separator.

The additive solution was injected at the wellhead in the two-phase flow by means of high-pressure metering pumps equipped with pulsation dampers, as the amount of scale deposited on the casing was very low.

Brine samples for chemical analysis were collected in the bypasses through sampling ports located downstream from the orifice plates.

Before using the inhibitors in the plant, preliminary batch tests were performed in order to check the compatibility of the additives with the geothermal brine by mixing the latter with each of the three products selected in the laboratory (Nadar 1602 and 4094; Degussa 1389).

Nadar 1602 addition induced instantaneous antimony and silica precipitation in the brine: it was therefore excluded from further tests

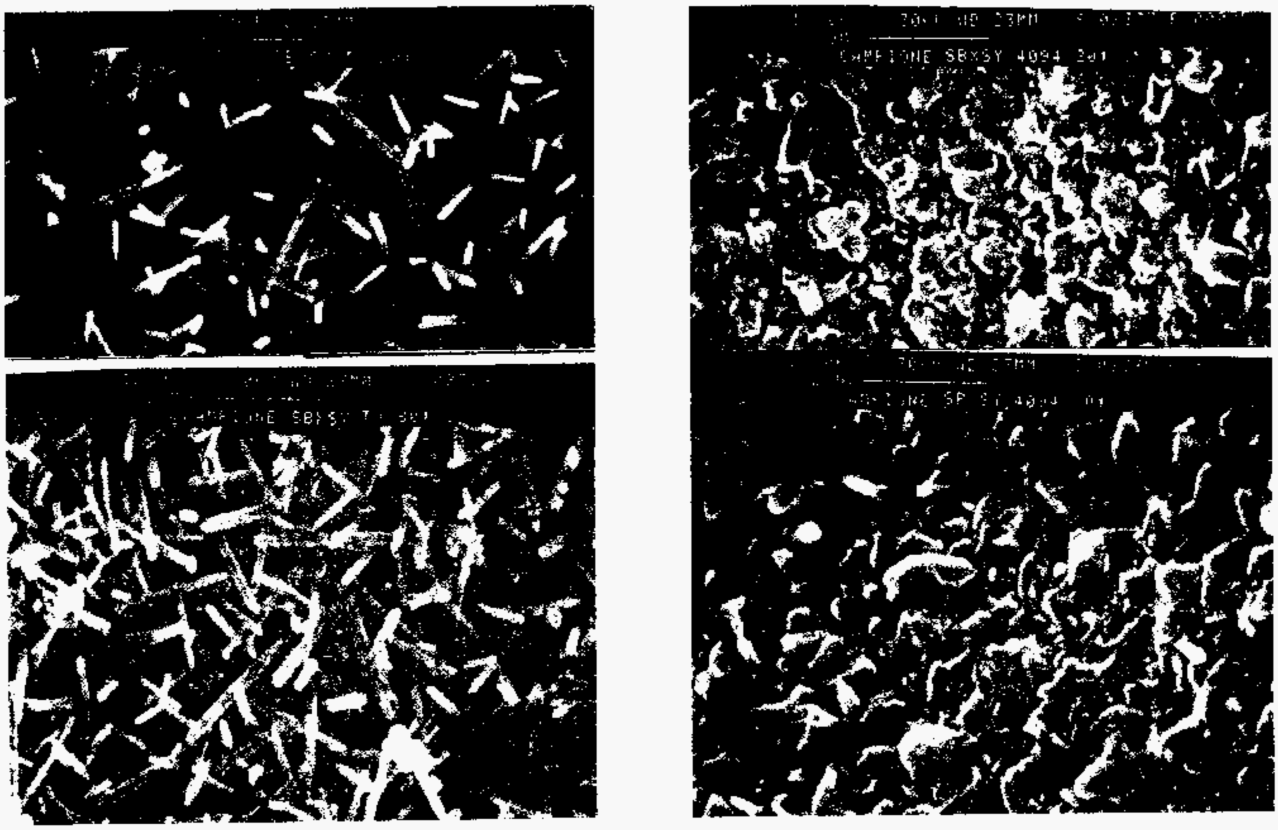


Figure 2. Crystal structures of precipitated antimony sulphide: acicular, from untreated solution (left) and granular, from solutions with inibitor addition (right).

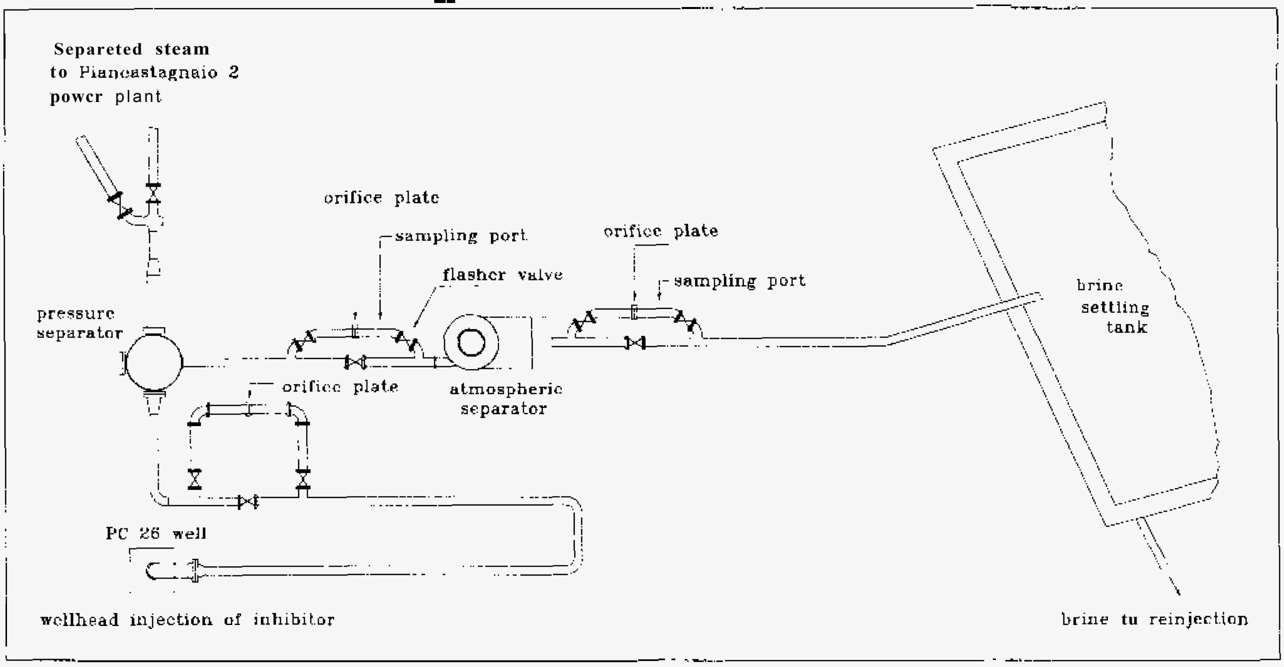


Figure 3. Separating plant installed at the Piancastagnaio 26 well

and used in a one-day run only in the plant, as subsequently described. The field tests were organized according to the following scheme:

- a blank or reference run, without the addition of any product, was first performed (run No. 1);
- a second run, with Degussa 1389 (at a concentration of 210 mg/l of separated liquid) injection at the well head, followed (run No. 2);
- a third run, with Nadar 4094 (at a concentration of 175 mg/l of separated liquid) injection at the well head, was then made (run No. 3).

During all the test runs, the bypasses were inspected every 3 weeks; the thickness of the deposits was measured and the scale sampled for analysis. No observation was possible, unfortunately, in the bypass upstream from the pressure separator, as its valves leaked even if shut after the blank test.

During these runs, the flow rate of the brine accompanying the steam produced by the well decreased substantially, thus making the test conditions nor uniform throughout the various runs. It was therefore decided to perform a short-term (one-day length) repetition of all the previous runs, including Nadar 1602 inhibitor.

A long-term test, about *3* months of duration with Nadar 4094 and 3 months with Degussa 1389, was then performed in order to check the effectiveness of the products in terms of plant reliability (runs Nos. 4 and *5*).

The well has subsequently been in operation since February 1993 on a continuous basis, using the separating plant with the bypasses removed, and with the addition of either 125 mg/l of Nadar 4094 or 150 mg/l of Degussa 1389 inhibitor at the wellhead (run No. *6*).

3.2 Results

In the blank test, scale deposits formed starting a few meters downhole the production casing and along all the plant piping down to the line connecting the atmospheric separator to the reinjection settling tank.

Upstream from the atmospheric separator, antimony sulphide (stibnite, Sb_2S_3) coprecipitated with amorphous silica, forming a hard black scale. Downstream, the scale was still black and was made up mainly of amorphous silica (Table 3).

During the blank test, the sampling valves became obstructed in a few days and had to be cleaned each time before being used.

In runs Nos. *2* and 3, with the addition of Degussa 1389 and Nadar 4094 inhibitors, no scale deposited upstream from the atmospheric flash (Table 3). Probably, the limited amount of scale observed during run No. 2 was due to loose scale formed during the previous blank run and coming from the pipes upstream

No obstruction of the sampling valves occurred in these runs with inhibitor addition.

Downstream from the atmospheric separator, scaling also occurred in the runs with inhibitor addition, due to the high silica supersaturation. The scale was orange in colour and the amount which was deposited using Degussa 1389 inhibitor was approximately the same as in the blank test. Using Nadar 4094 inhibitor, a somewhat larger amount of soft yellow scale was deposited in the atmospheric separator and in the reinjection line.

Comparisons *between* the behaviour of the two additives were difficult, however, because in this first series of runs the separated brine flow rate decreased and its composition was not constant, as previously mentioned (Table 4).

A more precise indication was therefore obtained during the following one-day runs, when the flow rate of the brine did not change significantly.

The chemical analyses of the brine at the outlet of the pressure separator clearly showed that the concentrations of both antimony and silica were lower, either without inhibitor or with Nadar 1602 addition, than in the runs with Nadar 4094 and Degussa 1389 addition (Figure 4).

The inhibitors, proved to be effective on antimony sulphide. The absence of silica deposition upstream and

Test run No.	Inhibitor	Downstream from the pressure separator		Downstream from the atmospheric separator	
		Thickness mm	Composition	Thickness mm	Composition
1	None	6	Stibnite + Silica	16	Silica + Stibnite
2	Degussa 1389	2	Stibnite + Silica	3	Silica + Stibnite (low)
3	Nadar 4094	*0*		5	Silica + Stibnite (low)
4	Nadar 4094	0		N A	
5	Degussa 1389	0		N/A	

Test run No.		1	2	3	4	5	6
Inhibitor		**None**	**Degussa 13891**	**Nadar 4094**	**Nadar 4094**	**Degussa 13891**	**Nadar 4094**
Inhibitor concentration	mg/l	-	210	275	90	130	125
Liquid flow rate	l/s	1.8	0.8	0.2	0.3	0.4	0.1
pH		6.84	6.48	5.4	5.5	5.7	6.7
Alkalinity	meq/l	3.72	5.5	12.8	8.14	13.3	33.8
Ca	mg/l	5.1	7.8	72.3	70.1	78.3	39.4
Mg	mg/l	<0.2	<0.2	<0.2	0.11	< 0.2	0.4
Na	mg/l	1454	1609	3377	3510	3110	2088
K	mg/l	316	376	830	739	552	363
Cl	mg/l	2520	2808	5686	6200	5860	3408
SO4	mg/l	10.9	18.4	24.8	21.6	19.4	76.1
H2S	mg/l	-	59.5	112	95	86	137
H3BO3	mg/l	13956	-	46202	47300	40000	30800
As	mg/l	57.4	73	-	201	176	157
SiO2	mg/l	1090	1357	869	975	948	384
Sb	mg/l	17.3	33.3	18.3	17.9	18.6	18

Figure 4. Chemical composition of the brine discharged by the pressure separator

downstream from the pressure separator, experienced during the tests with the use of additives, can be explained by the inhibition of the antimony sulphide precipitation, whose particles act as deposition nuclei for the amorphous silica.

The effectiveness of Nadar 4094 and Degussa 1389 inhibitors was ascertained in the long-term test (six months duration).

The results of this test confirmed those previously obtained: no scaling was detected in the line upstream from the atmospheric separator at the end of the test and the operation of the plant proved to be reliable.

It was therefore decided to use the inhibitors on a continuous basis during the production of the well.

The well and the separating plant have been operating smoothly and no scale deposition has been detected to date in the pressure separator. The problems related to valve operation and plant reliability have no longer been experienced.

4. CONCLUSIONS

The other wells drilled in the Piancastagnaio field showed chemical compositions slightly different from the ones of the PC-26 well and did not give rise, **as** was initially feared, to sulphide scaling. PC-26 is therefore the only well in production currently treated with chemical additives.

However, laboratory and field tests experience demonstrates that antimony sulphide precipitation can be prevented with the use of chemical additives.

It is therefore likely that the deposition of other kinds of sulphides (e.g. iron, lead), typical of other geothermal fields, may be inhibited with similar products, too.

Though no effort was undertaken during the tests to determine the minimum effective concentration of chemicals needed, this type of treatment proved to be economically effective, **thanks** also to the limited flow rate of brine to be inhibited (typically ranging from 0.2 to 1.4 l/s).

In fact, as the cost of both the effective inhibitors tested in the field is around 3 US$/kg, assuming a separated liquid flow rate of 0.5 l/s and an addition of 150 mg/l, the resulting cost of the treatment is only 0.8 US$/h.

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